

Appendix XI Organic Lead Test Method



1.0 Scope and Application.

1.1 This method is used to determine the sum of organic lead compounds ("organolead") in liquids, solids or sludges. The method detection limit for a 50 g sample is 0.5 µg/g (as lead); the method detection limit for 200 ml water samples is 0.1 mg/l (as lead).

2.0 Summary of Method.

2.1 Organolead is separated from the sample matrix by extraction with xylene. The organolead in the extract is reacted with Aliquat 336 and iodine and the solution is made up to volume with MIBK. Lead contained in this mixture is determined by flame atomic absorption spectrometry (FAAS). If the original sample is completely soluble in xylene, the extraction step is omitted.

3.0 Safety.

3.1 Some organic lead compounds are volatile and toxic. Therefore, samples must be processed in a well-ventilated hood. Antiknock lead compounds are particularly poisonous and must not be inhaled or ingested or come into contact with the skin. Antiknock lead compounds should never be exposed to elevated temperatures (above 50°C) or to acids and oxidizing agents. Whenever organic lead compounds are handled outside of a well-ventilated hood, protective respiratory equipment, protective clothing and rubber gloves must be worn. The material safety data sheets (MSDS) for organolead standards must be read.

3.2 The solvents used in this method are flammable. Proper precautions must be taken to prevent contact with sparks or open flames (other than the AAS flame).

4.0 Interferences.

4.1 To reduce loss of organic lead compounds which are very volatile and sensitive to oxygen, samples must not be exposed to elevated temperatures or to air for extended periods of time. Such losses shall be minimized by adhering to the sample collection, preservation and handling procedures in subdivisions 7.2 - 7.4 and 8.1.1 of this appendix.

4.2 If the samples are moist, there may be poor wettability with xylene.

5.0 Apparatus and Materials.

5.1 flame atomic absorption spectrometer (FAA spectrometer) with background corrector and recorder or integrator;

5.2 lead hollow cathode lamp or electrodeless discharge lamp;

5.3 nebulizer with impact bead; the standard rubber gasket in the nebulizer must be replaced with a cork gasket because the organic solvents used in this method attack rubber;

5.4 air, acetylene and appropriate AAS burner head;

5.5 erlenmeyer flasks, 250 ml and 100 ml, with ground glass stoppers;

5.6 mechanical shaker;

5.7 glass filter funnel and filter paper (Whatman #40, #42 or equivalent);

5.8 separatory funnels, 250 ml capacity;

5.9 volumetric flasks, 250 ml, 100 ml, and 50 ml.

6.0 Reagents.

All solvents and reagents must be at least analytical reagent grade, if available.

6.1 xylene (use p-xylene if available);

6.2 methyl isobutyl ketone (MIBK, 4-methyl-2-pentanone);

6.3 iodine solution: dissolve 3.0 g of elemental iodine in toluene and make up to 100 ml with the same solvent. Store in a brown bottle in a refrigerator;

6.4 Aliquat 336 (Tri-capryl methyl ammonium chloride), available from Aldrich, Milwaukee, WI, or from McKesson Co., Minneapolis, MN. Aliquat is a registered trademark of Henkel Corporation. Prepare two solutions, one containing 10 percent weight to volume ratio (w/v) and one containing 1 percent (w/v) in MIBK. Store in a refrigerator;

6.5 anhydrous sodium sulfate, granular;

6.6 lead chloride, crystals. Dry at 105°C for 3 hours before use.

6.6.1 Prepare a stock solution containing 1000 mg/l of lead (Pb) by dissolving 0.3356 g of lead chloride in 10 percent Aliquat 336 in MIBK and dilute to 250 ml. Store in a brown bottle in a refrigerator.

6.6.2 Prepare an intermediate Pb standard by pipetting 10 ml of the stock standard into a volumetric flask and diluting to 100 ml with a 40 percent volume to volume ratio (v/v) solution of xylene in MIBK. Store in a brown bottle in a refrigerator;

6.7 sodium chloride (NaCl).

7.0 Sample Collection, Preservation, and Handling.

7.1 For safety precautions, see subdivision 3.0 of this appendix.

7.2 Liquid samples must be collected in amber glass bottles (preferably 500 ml size) with Teflon-lined caps without leaving any headspace. During sampling, contact of the sample with air must be minimized.

7.3 Solid samples must be collected in glass jars (preferably 250 ml size) with airtight, Teflon-lined lids. The jars must be filled to capacity.

7.4 All samples must be transported and stored at refrigerator temperature (approximately 5°C.).

8.0 Procedure. The order of addition of the reagents must be followed explicitly. Aliquat 336 must not be added before the addition of iodine because it retards the formation of the alkyl lead iodide-Aliquat 336 complex, giving erroneous results.

8.1 Extraction of Solid and Sludge Samples.

8.1.1 Weigh out (to the nearest 0.1 g) about 50 g of homogenized sample into an Erlenmeyer flask, add 100 ml of xylene, stopper the flask and shake on a mechanical shaker for 30 minutes (min). The extraction efficiency may vary depending on the moisture content of the sample. Stirring of the sample with a mechanical or magnetic stirrer must not be substituted for shaking since it can result in loss of organolead due to oxidation by air oxygen. For the same reason, extraction times of more than 30 min must be avoided.

8.1.2 After extraction, filter the xylene phase through filter paper holding about 10 g of anhydrous sodium sulfate.

8.1.3 Pipet 20 ml of MIBK and 20 ml of the filtered extract into a 50 ml volumetric flask and mix.

8.1.4 To the same flask, add 0.1 ml of iodine solution and mix again. Let react for approximately 1 min.

8.1.5 To the same flask, add 5 ml of 1 percent Aliquat 336 in MIBK, dilute to volume with MIBK and mix.

8.2 Extraction of Liquid Samples.

8.2.1 Place 200 ml of the sample and 50 ml of xylene into a separatory funnel, close the funnel and shake for 1 - 2 min. Allow 5 - 10 min for phase separation. If less than 200 ml of sample is available, the miscibility with xylene may be tested with a smaller aliquot.

8.2.2 If a single liquid phase is obtained (i.e., if the sample is completely soluble in xylene), discard the sample/xylene mixture and pipet 20 ml of neat sample into a 50 ml volumetric flask, add 20 ml of MIBK, mix, and continue as described in subdivision 8.1.4 above.

8.2.3 If an emulsion is obtained which requires more time for phase separation, add about 5 g of NaCl to the separatory funnel, shake briefly, and let the mixture settle for 20 min.

8.2.4 After separation of the xylene phase from the sample solvent phase (e.g., water), drain off the lower phase into a second separatory funnel and collect the xylene extract in a 100 ml flask with ground glass stopper.

8.2.5 Add 25 ml of xylene to the sample solvent phase, shake for 1-2 min and allow 5 - 10 min for phase separation.

8.2.6 Repeat subdivision 8.2.4, adding the xylene phase to the first extract. Then repeat subdivisions 8.2.5 and 8.2.4 with another 25 ml of xylene.

8.2.7 Filter the combined extract through filter paper holding about 10 g of anhydrous sodium sulfate.

8.2.8 Pipet 20 ml of MIBK and 20 ml of the filtered extract into a 50 ml volumetric flask and mix. Continue as described in subdivision 8.1.4 above.

8.3 Standard and Blank Preparation.

Prepare a blank and a minimum of three appropriate working standards from the intermediate organolead standard containing 100 mg/l as Pb.

8.3.1 Place 40 ml of xylene into a 100 ml volumetric flask and add the correct amount of the 100 mg/l standard to prepare the desired concentration.

8.3.2 Immediately add 0.2 ml of iodine solution and mix well.

8.3.3 Add 10 ml of 1 percent Aliquat 336 solution, dilute to volume with MIBK and mix well.

8.3.4 The blank is prepared in the same way as the calibration standards (subdivisions 8.3.1 - 8.3.3 of this appendix), except that no organolead intermediate standard is added.

8.4 Flame Atomic Absorption Measurements.

Since certain organolead compounds are very volatile, their vapors may remain in the nebulizer or drain tube for considerable periods of time and affect subsequent readings. Therefore, sufficient time must be allowed between readings for all vapors to clear the system. Analyzing a blank between samples can check on the system.

8.4.1 The FAA spectrometer is set up according to the manufacturer's instructions. The nebulizer is equipped with the impact bead and a cork gasket is installed. Ensure that the drain tube to the waste container drains properly. Tygon tubing is affected by the organic solvents used in this method and drainage properties will be different from those observed with aqueous samples. If desired, a waste container dedicated to receive organolead waste may be connected.

8.4.2 While aspirating water into the flame, adjust the acetylene flow to 8.5 l/min and the air flow to 25 l/min.

8.4.3 Aspirate MIBK containing 40 percent xylene into the flame, reduce the acetylene flow to approximately 4.8 l/min and fine adjust to produce an even flame with no yellow luminescence.

8.4.4 Measure the absorbance of the method blank, working standards, and samples.

8.4.5 If sample readings fall outside the calibrated range, the solutions to be aspirated into the nebulizer must be diluted with a 40 percent (v/v) solution of xylene in MIBK and analyzed again.

9.0 Calculations.

Depending on the type of sample analyzed and the method of sample preparation, one of the following three formulas is used to calculate the concentration of organolead in the sample:

9.1 solid and sludge samples:

$$\text{Conc (Mg/g)} = \text{FAA-Result (mg/l)} \times \frac{100\text{ml}}{W \text{ (g)}} \times \frac{50\text{ml}}{20\text{ml}} \times F$$

where W (g) is the sample mass in grams (usually 50 g) and F is the dilution factor;

9.2 liquid samples not soluble in xylene:

$$\text{Conc (mg/l)} = \text{FAA- Result (mg/l)} \times \frac{100\text{ml}}{V \text{ (ml)}} \times \frac{50\text{ml}}{20\text{ml}} \times F$$

where V (ml) is the sample volume in ml (usually 200 ml) and F is the dilution factor;
 9.3 xylene-soluble liquid samples:

$$\text{Conc (mg/l)} = \text{FAA-Result (mg/l)} \times \frac{100\text{ml}}{V \text{ (ml)}} \times \frac{50\text{ml}}{20\text{ml}} \times F$$

where V (ml) is the sample volume in ml (usually 20 ml) and F is the dilution factor.

10.0 Quality Control.

10.1 Analyze a method blank along with each batch of ten samples (or less). If the blank indicates a significant contamination (more than twice the method detection limit), repeat all procedures with samples and blank.

10.2 Analyze a duplicate sample with each batch of ten samples or less.

10.3 Analyze a spiked sample with each batch of ten samples or less. The level of spiking must be about twenty times the method detection limit. If the sample contains measurable organic lead, the spike level must be at least four times the measured level.

10.4 Leaded gasoline with known concentration of organolead must be used as spiking solution for all sample types.

11.0 Method Performance.

11.1 The analysis of four replicates of water samples spiked with leaded gasoline gave a mean result of 3.23 mg/l, a standard deviation of 0.032 mg/l, and a relative standard deviation (RSD) of 0.99%. The mean recovery was 3.23 mg/l for a recovery of 67.7%.

11.2 The instrument detection limit (IDL) was determined by the analysis of eleven replicates, blanks and standards. The IDL was based on three times the standard deviation which was 0.09 mg/l.

11.3 The analysis of six replicates of soil samples spiked with gasoline gave a mean result of 3.16 mg/kg, a standard deviation of 0.025 mg/kg, and a RSD of 0.80%. The mean recovery was 3.16 mg/kg for a 66.2% recovery.

NOTE: Authority cited: Sections 208 and 25141, Health and Safety Code. Reference: Section 25141, Health and Safety Code.

HISTORY

1. New section filed 5-24-91; effective 7-1-91 (Register 91, No. 22).